Drying Leather with Vacuum and Toggling Sequentially

by

Cheng-Kung Liu,* Nicholas P. Latona, and Joseph Lee
*U. S. Department of Agriculture,** Agricultural Research Service,*
Eastern Regional Research Center
600 E. Mermaid Lane, Wyndmoor, PA, 19038

Abstract

We investigated a drying method that will enable leather to be dried under vacuum and stretch sequentially to improve area yield. Vacuum drying offers fast speed at a low temperature, which would be advantageous to heat-vulnerable chrome-free leather. Adding a toggle action after vacuum drying could significantly increase area yield. Using a statistical experimental design, we formulated regression models describing how drying variables affect mechanical properties and area yield of chrome-free leather tanned with glutaraldehyde. An effort was also made to estimate the effects of conditioning, staking, and drum milling on the area retention gained by toggle stretching. This study showed that the direction the stretch was applied had a significant effect on the area retention. Results also indicated that conditioning and staking have little effect on area retention, whereas the drum milling caused a significant drop in area retention. Our study also showed under an optimal drying condition, a 12% increase in area yield with good properties can be achieved.

Resumen

Hemos investigado un método de secado que permitiría al cuero ser secado al vacío y posteriormente estirado para mejorar el rendimiento superficial obtenible. El secado al vacío ofrece velocidad en el procesamiento a bajas temperaturas, lo cual sería ventajoso para cuero exento de cromo el cual no es muy resistente al calor. Añadiendo la acción de estirado por ganchos posteriormente al secado al vacío, podría significativamente aumentar el rendimiento superficial. Por medio de un diseño experimental estadístico para modelos de regresión que describen como las variables del secado afectan las propiedades mecánicas así cómo el área obtenible en cueros exentos de cromo curtidos al glutardialdehído. Un esfuerzo también se efectuó para estimar los efectos del acondicionado, ablandado y fulonado sobre la retención del área adicional obtenida por medio del estiramiento por medio de ganchos. Este estudio demostró que la retención del área adicional dependió de la orientación del estiramiento. Los resultados también demostraron que el acondicionado y ablandamiento tuvieron poco efecto en retención de área adicional obtenida, mientras que el fulonado ocasionó una significativa merma en el área adicional obtenida. Nuestro estudio demostró que bajo óptima condición de secado, un 12% de incremento en área es obtenible manteniendo buenas propiedades físicas a la vez.

INTRODUCTION

One of the important mechanical operations in the leather making process is the removal of excess water from leather-- drying. Leather acquires its final texture, consistency and flexibility in the drying operations. Vacuum drying has become one of the most popular drying methods in recent years for leather manufacture because of its fast drying speed and reduced space requirement.[1, 2] We previously established a predictive vacuum drying model for chrome-free leather (drying variables vs. drying rate and physical properties of leather, from experimental physical and chemical testing data).[3] The drying constant indicates that chrome-free leather dries faster than chrome-tanned leather. The model formulated for the drying rate may benefit the leather industry in estimating the right drying parameters to dry leather. Furthermore, we experimented with two-dimensional toggling (biaxial stretching) during vacuum drying. This may possibly be the most desirable drying method for this particular type of leather, because it results in an improved area yield and better mechanical properties due to a lower drying temperature. We explored this composite drying method and investigated how drying variables affect the drying rate and mechanical properties of chrome-free leather tanned with glutaraldehyde.[4] A tanning process using glutaraldehyde was developed in the early 1960's by Filachione *et al*. in the Eastern Regional Research Center (ERRC).[5-9] It has become the most commonly used alternative tanning agent to chrome salts, because it is less expensive, is readily available and is highly soluble in aqueous solution. Results of our composite drying studies showed that the stretch applied in a drying operation significantly affects stiffness and area yield. We observed that biaxial stretch increases tensile strength but has less effect on toughness. Our study also showed that tensile strength increases with apparent density and decreases with drying rate. Under an optimal drying condition, a 16% increase in area yield with good properties can be achieved.[4] However, this drying method needs a very sophisticated stretching frame that would allow leather to be toggled and stretched during the vacuum drying, which is a major hurdle for the leather industry to adopt this technology. In this study, we designed a different drying method that could be applied by tanneries without incurring extra investment in a new toggle frame. This system will enable leather to be dried under vacuum and stretch sequentially to improve the area yield. Adding a toggle action after vacuum drying could significantly increase the area yield. By using a statistical experimental design, we investigated how drying variables affect mechanical properties and area yield of chrome-free leather. An effort was also made to estimate the effects of conditioning, staking, and drum milling on the area retention gained by toggle stretch.

EXPERIMENTAL

Materials and Procedures
Bovine wet white tanned with glutaraldehyde was obtained from a domestic tannery. Square samples 45.7- x 45.7-cm were cut out near the standard butt test area (ASTM D2813-03) and applied the retanning and fatliquoring process previously reported for the preparation of chrome-free samples.[2] The leather was drained, washed at 50°C, drained again and set-out. For monitoring the change in area, a 30.5- x 30.5- cm square was drawn on the leather samples before vacuum drying.

Apparatus
The samples were dried according to conditions that were carefully designed as described later. We used a Cartigliano vacuum drying machine located in the ERRC pilot plant tannery. The vacuum pressure for the drying experiments was maintained at 0.8 bar, which equals 20 kPa absolute pressure. It is a typical pressure used in a vacuum drying operation. The samples were vacuum dried and then toggled for 30 minutes at 49°C according to the ratio specified in the statistical experimental design as described later. Finally the samples were placed in a conditioning room and equilibrated at 23°C with 50 percent RH. The samples were then wet back and conditioned overnight and then passed through a Molissa staking machine at a medium setting (model 16370, Strojosuit, Czechoslovakia) twice at a rate of 1.63 meters/min (5.3 ft/min). Last, the samples were milled in a drum for 6 h at 16 revolutions per min.

Measurements
The area retention or area yield was followed and calculated by measuring the area after toggle stretch (A1), conditioning (A2), staking (A3) and drum milling (A4), and then comparing them to the original area, i.e. before the drying experiments (A0); the equation for calculating area retention can be written as: A/A0. Mechanical property measurements included tensile strength, elongation and fracture energy. Tensile strength is the stress in tension that is required to fracture the leather. Fracture energy is defined as the energy needed to fracture leather samples. This physical quantity is sometimes mentioned as "toughness". Dogbone shaped leather samples were cut near the standard test area parallel and perpendicular to the backbone as described in ASTM D2813-03. These properties were measured with a grip separation of 6.7 cm and a 5 cm/min strain rate (crosshead speed). An upgraded Instron mechanical property tester (Instron, Norwood, MA), model 1122, and Testworks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. Each test was conducted on five samples in each direction to obtain an average value.

Experimental Design

A central composite design was applied to arrange drying conditions, thereby establishing regression models. This experimental design was developed by Box and Hunter[10] and is the most widely used design for fitting a second-order model. The four factors selected were drying temperature (x'_1) and drying time (x'_2) applied in vacuum drying and stretch % parallel to the backbone (x'_3) and stretch % perpendicular to the backbone (x'_4) on the toggle screen. To simplify the calculations, the independent variables were transformed to coded variables: x_1, x_2, x_3 and x_4 by means of the following formulae: $x_1 = (x_1'-60)/10$, $x_2 = (x_2'-10)/5$, $x_3 = (x_3'-10)/10$ and $x_4 = (x_4'-10)/10$. It is desirable to visualize the relation between the response and the factor levels geometrically. Response surfaces (a surface plot of the resultant property as a function of multiple independent variables) were constructed based on the regression equation, using graphics and data analysis software Axum version 6 developed by MathSoft, Inc, Cambridge, MA.

RESULTS AND DISCUSSION

The regression equations of area retention and major physical properties were derived as a function of experimental variables with the multiple correlation coefficient (R),[11] which is a measure of the strength of a multiple regression model, are shown in Table I.

TABLE I

The regression models and multiple correlation coefficients (R)

	Multiple Regression Equations	R
Area Retention	1.215997 - 0.062085*X1 - 0.02506*X2 + 0.041674*X3 + 0.043838*X4 - 0.056577*X1*X1 - 0.018508*X1*X2 - 0.015157*X1*X3 - 0.001239*X1*X4 - 0.001053*X2*X2 + 0.004254*X2*X3 - 0.001252*X2*X4 + 0.006065*X3*X3 + 0.013526*X3*X4 + 0.010194*X4*X4	0.92
Tensile Strength (MPa)	10.90696 - 0.586406*X1 - 0.099094*X2 + 0.120853*X3 - 0.085228*X4 + 0.419537*X1*X1 + 0.034054*X1*X2 - 0.563367*X1*X3 + 0.268342*X1*X4 - 0.356063*X2*X2 + 0.008742*X2*X3 + 0.051908*X2*X4 + 0.658862*X3*X3 + 0.717204*X3*X4 + 0.036299*X4*X4	0.64
Elongation (%)	58.40827 - 5.698989*X1 - 0.513352*X2 - 0.450823*X3 - 2.604944*X4 - 2.212786*X1*X1 - 0.255384*X1*X2 - 2.374216*X1*X3 + 0.785603*X1*X4 + 0.720402*X2*X2 + 1.057066*X2*X3 + 1.207497*X2*X4 + 3.578089*X3*X3 + 1.844553*X3*X4 + 0.114052*X4*X4	0.81
Fracture Energy (J/cm³)	2.567033 - 0.275749*X1 - 0.02231*X2 - 0.012982*X3 - 0.147568*X4 + 0.067068*X1*X1 + 0.04024*X1*X2 - 0.30144*X1*X3 + 0.075177*X1*X4 - 0.058182*X2*X2 + 0.047602*X2*X3 + 0.06786*X2*X4 + 0.404881*X3*X3 + 0.335565*X3*X4 + 0.005443*X4*X4	0.71
Grain Break	3.916667 - 0.5*X1 - 0.25*X2 - 0.166667*X4 - 0.708333*X1*X1 - 0.125*X1*X2 - 0.125*X1*X3 + 0.25*X1*X4 - 0.208333*X2*X2 - 0.125*X2*X4 - 0.333333*X3*X3 - 0.125*X3*X4 - 0.458333*X4*X4	0.93

Note: X_1=Temperature, X_2=Drying Time, X_3=Stretch parallel to backbone, X_4=Stretch perpendicular to the backbone line.

Area Retention

Shrinkage is the most recognized phenomenon in the leather drying process. Like most other hydrophilic materials, leather shrinks during the drying process and produces less area yield. The shrinkage of hydrophilic materials after the removal of water is a well-known behavior. During water removal, the space originally occupied by water is slowly squeezed and decreased. The water removal is driven by the internal pressure release and therefore the materials shrink. Shrinkage produces less area yield and is the most common problem involved in the leather drying process. The price of a piece of leather is determined by its area. The importance of knowing the effect of leather making conditions on the resultant area yield cannot be over-emphasized enough. Although vacuum drying offers many advantages as mentioned before, many tanneries are still hesitant to use this drying method and toggle drying therefore is still widely used. The current drying method used in this study actually combines toggling and vacuum drying, in which the leather is dried in a vacuum oven and then stretched on the toggle screen to dry for an additional 30 min. By using this drying method, one may obtain the advantages of both methods. Figure 1 is a 3D response surface based on the regression models listed in Table I that illustrates the effects of stretch % on the dimensional increase in terms of area retention (A1/A0), where the original area of the leather drying samples is noted as A_0 and A_1 is the area after toggling. Although stretching in both parallel (X) and perpendicular (Y) to the backbone increases area retention, the results however showed the increase stretch % perpendicular to the backbone (Y) yielded more area increase compared to stretch % parallel to the backbone (X). This is probably due to the anisotropic nature in the alignment of the fiber bundles of bovine hide in which the fibers tend to align in one direction (parallel to the backbone) and are therefore more resistant to stretching in that direction.
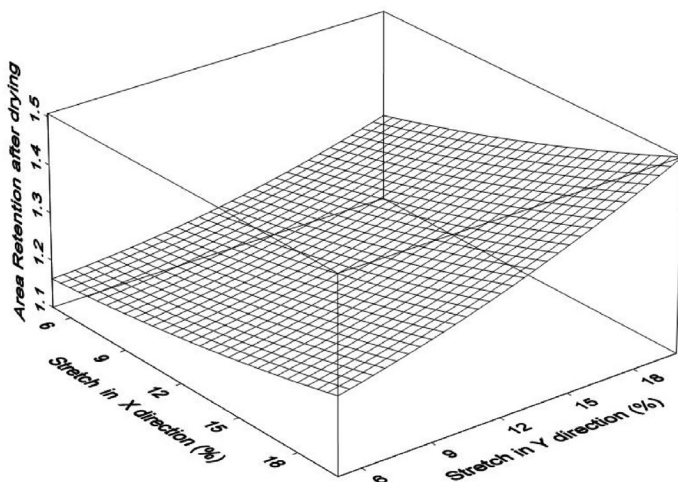

Figure 1. Area retention as a function of stretch %.

A 3-D response surface of % area retention as a function of drying temperature and time is shown in Figure 2. It demonstrates that a higher vacuum drying temperature will increase the area retention until around 58°C, the area retention starts to drop as the temperature rises further. On the other hand, results show that the area retention decreases with drying time. This can be attributed to a longer vacuum drying time may lead to an increase in the residual stress and consequently the elastic memory that was induced by the toggling action during stretching. Thus, during conditioning, the leather shrinks more and consequently has less area retention.
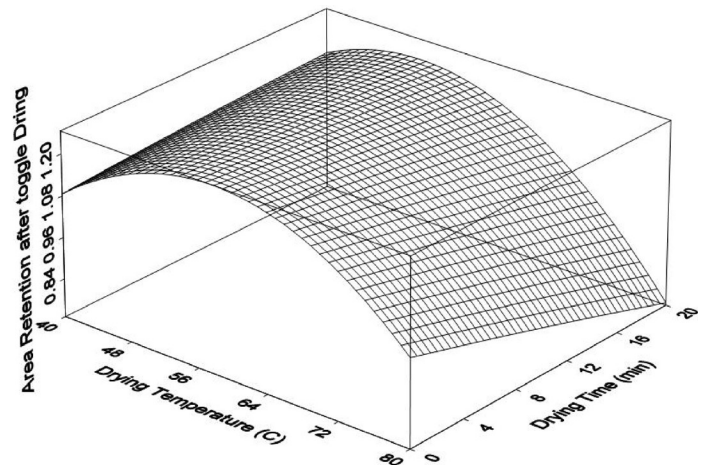

Figure 2. Area Retention versus drying temperature and time.

It should be stressed that the area retention value refers to the ratio of area change after toggle drying (A1), each additional process such as conditioning (A2), staking (A3) and drum milling (A4) may cause some change in area retention, which will be discussed later.

Effects of Staking and Drum Milling

The processing of hides into leather is a very complicated procedure that requires a precise combination of various chemical and mechanical operations. After the leather has been dried following the tanning process, and even though the leather fibers had been lubricated with fatliquors, without additional mechanical force, the fibers of the leather can still stick together, leaving the leather rigid and hard. Therefore the leather must be physically conditioned by staking and/or milling. Staking is a mechanical method that increases the pliability and softness of the leather. The hide travels through the machine on a conveyor belt and is pounded by several thumb-sized rounded pins that stretch the fibers in every direction, thus separating the fibers and softening the leather. We previously studied the interaction between staking and fatliquoring for vacuum-dried leather.[12] We discovered that staking actually stiffens the leather if it has not been treated with fatliquor. The softening action of staking only becomes effective after the fatliquor concentration reaches a certain

level. After being staked, the leather will usually go through the milling process to further soften the leather. Milling is a physical softening process in which leather is tumbled in a dry drum fitted with wood dowels with atomized moisture injected into the tumbler. An acceptable softness can generally be obtained by careful control of the drum speed, time and humidity inside the drum. Milled leather often offers superior feel and easy break-in for gloves and shoes.

Figure 3 demonstrates the effects of conditioning, staking and drum milling on the area retention of leather. This figure indicates that the conditioning and staking has very little effect on the area retention measured after toggle drying. In contrast, drum milling significantly decreased the area gained from the toggle action as shown in Figure 3. According to the regression equation, after drum milling, the resultant leather loss is about 44% of the area retention originally obtained from the toggle action. This can be ascribed to the fiber opening effect caused by drum milling, leading to area shrinkage. As shown in a previous report, electron scanning microscopic observation showed milled leather fibers are well separated from each other, whereas the non-milled sample fibers are still stuck together.[13] Although it causes area shrinkage, an opened fiber structure is needed for gaining softness in leather, which is one of the many important properties for upholstery leather.

Tensile Strength

Tensile strength is one of the most important qualities of leather and strongly governs its end use. Figure 4 shows a 3-D response surface of the resultant tensile strength as a function of drying temperature and time simultaneously. Collagen materials such as leather in general have very poor heat resistance. Figure 4 demonstrates that the higher drying temperature impairs tensile strength significantly. The higher temperature drying not only shrinks the leather, but also makes the leather fibers brittle and stiff, thereby decreasing the tensile strength. The effects of drying time, on other hand, are complicated, as shown in Figure 4, the tensile strength increases with drying time until about 12 minutes and then it starts to decrease with drying time. This is probably ascribed to the leather is drier due to the longer vacuum drying times, thereby increasing the amount of force to toggle the leather to the desired stretch %. Thus the tensile strength is higher due to an increase in the orientation of the leather fibers caused by a higher toggle tension. However, when the drying time is longer than 12 minutes, the leather can become too brittle and the subsequent toggle action could break the fiber bundles and result in lower tensile strength.

Elongation

Figure 5 shows a 3-D response surface of the resultant elongation (as an indication of extensionability) as a function of drying temperature and time. It demonstrates that the extensionability of leather, in general, decreases steadily as the
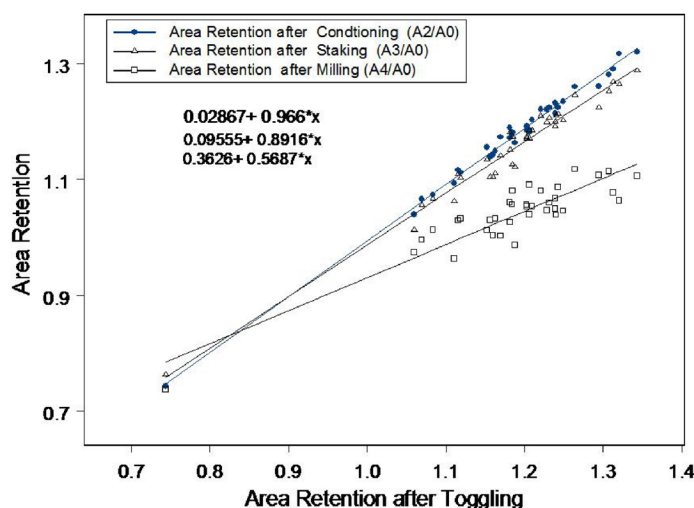

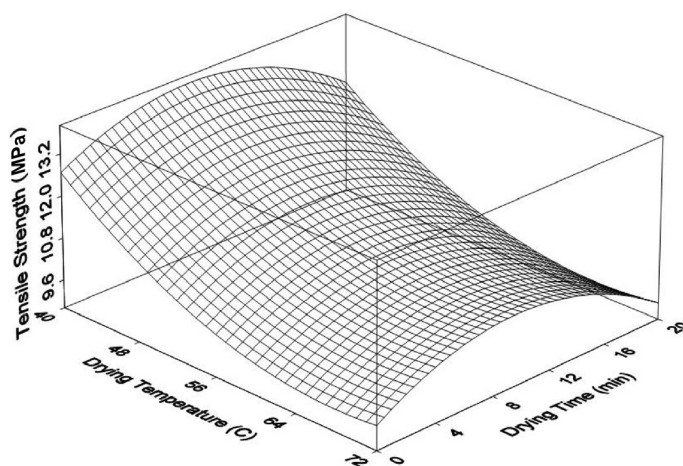Figure 3. Area Retention after (a) conditioning, (b) staking and (c) drum milling

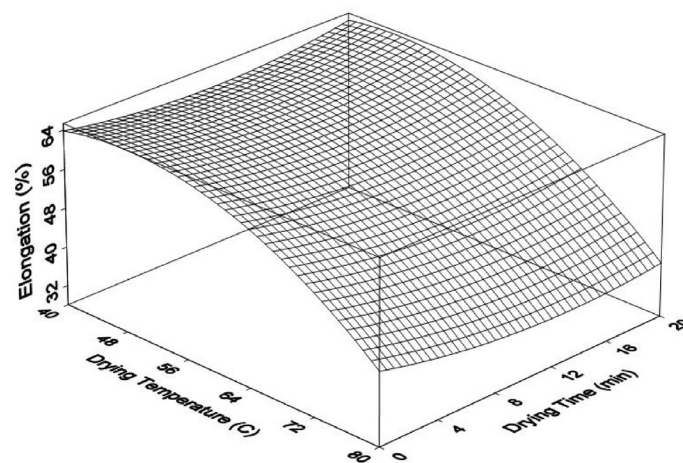Figure 4. Tensile Strength as a function of drying temperature and time.

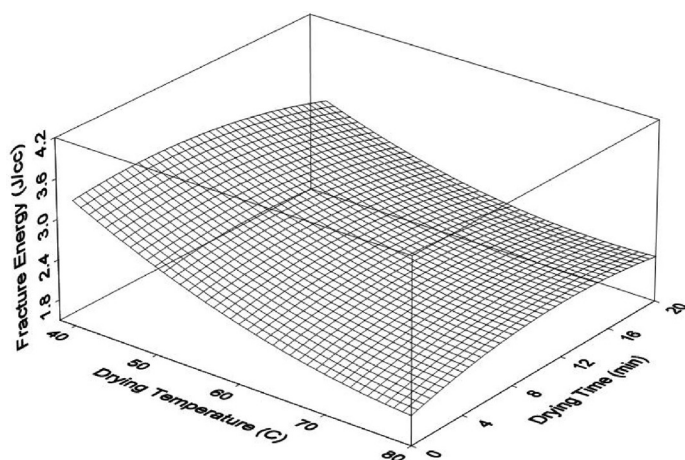Figure 5. Elongation vs. drying time and temperature.

Figure 6. Fracture energy as a function of drying temperature and time.

drying temperature increases. On the other hand, it appears that drying time has little effect on elongation. High temperature causes brittleness of leather and therefore lower elongation.

Fracture Energy--Toughness

Fracture energy has been described in a previous report as a physical quantity associated with the energy required to fracture leather.[14] We have characterized the toughness of leather by measuring the energy needed to fracture a sample, which is obtained by integrating the area under the force-elongation curve. Previously we have reported that contrary to tensile strength, the sampling angle shows little effect on the toughness. Our previous investigation also demonstrated a strong correlation between tear strength and toughness. Good toughness reflects a superior balance of strength and flexibility with good deformability, thereby minimizing the stress concentration and yielding a better tearing strength. Figure 6 shows a 3-D plot of resultant fracture energy as a function of drying time and temperature simultaneously. It demonstrates

that, similar to the tensile strength, the toughness of leather steadily decreases as the drying temperature increases. It also shows that the drying time has less effect on the resultant toughness of leather.

If we set the boundary conditions of the mechanical properties required in tanneries as follows: tensile strength greater than 10 MPa, elongation greater than 40% and less than 80%, Young's modulus less than 25 MPa, fracture energy greater than 2 J/cm³ as shown in Table II, a 1.12 area retention after drum milling (12% increase in area yield) can be achieved using the following conditions: drying temperature of 60°C, drying time of 15 min, 10% stretch in the X direction and 10% stretch in Y direction.

Grain break

Grain "break" is characterized by the wrinkles formed on the surface of the leather when it is bent or flexed inward. It is a unique term used in the leather industry. There are two types of grain break: a fine break and a coarse break. "Fine break" has many fine wrinkles per square inch, which in fact is more desirable for today's tanners. Most tanners want to produce the finest break possible in their product. A "coarse break" on the other hand will have fewer wrinkles and be more pronounced, giving the grain surface a loose appearance. Coarse break often is caused by poor tannery processing in the beaming, tanning and retanning or stale hides.[15] Grain break is also a naturally occurring characteristic of the hide and area wise the butt has a finer break than the shoulder and belly. To have fine break, it is necessary for tannery processes to prevent the fibrils from sticking together tightly on the grain surface. Higher amounts of oil in the grain layer will yield a finer break. We manually assessed the break of the samples using an arbitrary scale having five levels of break ranging from 5, fine (the best), to 1, coarse (the worst). As demonstrated in Figure 7, there is a very complicated relationship between drying variables and grain break. This figure indicates there is an optimum condition at around the

TABLE II

Optimum Drying Condition

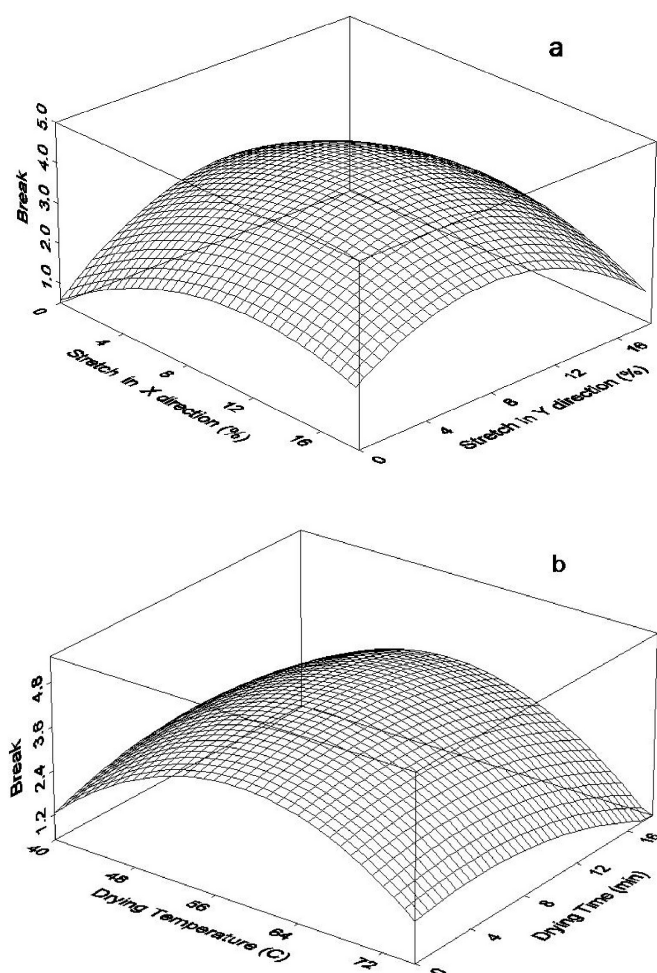| Temperature °C	Time (Min)	Stretch X (%)	Stretch Y (%)	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)	Toughness (J/cm3)	Area Retention (A4/A0)
60	15	10	10	11.6	62	6.0	2.8	1.12
60	15	20	10	12.9	63	7.8	3.5	1.11
60	15	10	20	10.7	49	8.9	2.1	1.11
60	20	15	15	13.3	71	4.3	3.9	1.08

Figure 7. Break (a) as a function of stretch %, (b) drying temperature and time.

center point of the experimental design that is: drying temperature 60°C, drying time 15 min, and stretch both directions 10% in toggle drying.

Conclusions

Our objective for this drying research is to obtain an improved drying method by combining vacuum and toggle in the leather drying process without expensive changes in equipment. Vacuum drying offers fast speed and low temperature drying that particularly is advantageous to chrome-free leather, since it often has a lower denaturation temperature. Adding toggle stretching after vacuum drying can increase area yield. However, drum milling may lead to a significant loss in area yield. This 2-step drying (vacuum then toggle) showed an area increase as high as 12% even after drum milling.

References

1. Leather Facts, 3rd edition, New England Tanners Club, Peabody, MA, p 21, 1994.
2. Liu, C.-K., Latona, N. P., and Lee, J. A drying study for glutaraldehyde-tanned leather. *JALCA* **100**, 8-15, 2005.
3. Liu, C.-K., Latona, N. P., and Cooke, P. Effects of stretch and drying rate on chrome-free leather. *JALCA* **101**, 330-335, 2006.
4. Liu, C.-K., Liu, L.S., Latona, N. P., Neil M. Goldberg., and Cooke, P. H. Composite drying with simultaneous vacuum and toggling. *JALCA* **104**, 131-138. 2009.
5. Fein, M. L., Harris, E. H. Jr., Naghski, J., and Filachione, E. M.; Tanning with glutaraldehyde. I. Rate studies. *JALCA* **54**, 488-502, 1959.
6. Filachione, E. M., Fein, M. L., Harris, E. H. Jr., Luvisi, F. P., Korn, A. H., Windus, W., and Naghski, J.; Tanning with glutaraldehyde. II. Properties of the leathers. *JALCA* **54**, 668-679, 1959.
7. Fein, M. L., Filachione, E. M., Naghski, J., and Harris, E. H. Jr.; Tanning with glutaraldehyde III. Combination tannages with chrome. *JALCA* **58**, 202-221, 1963.
8. Filachione, E. M., Fein, M. L., and Harris, E. H. Jr.; Tanning with glutaraldehyde. IV. Use in side leather. *JALCA* **59**, 378-402, 1964.
9. Filachione, E. M., Fein, M. L., and Harris, E. H. Jr.; Tanning with glutaraldehyde. *JALCA* **59**, 281-292, 1964.
10. Box, G. E. P., and Hunter, J. S.; Multifactor experimental designs for exploring Response Surfaces. *Ann. Math. Stat.*, **28**, 195-241, 1957.
11. Freund, R. J., Wilson, W. J.; Statistical Methods. p 369, Academic Press, San Diego, CA, 1993.
12. Liu, C.-K., Latona, N. P., and DiMaio, G. L.; Staking and its interaction with fatliquoring on vacuum-dried leather. *JALCA* **96**, 243-254, 2002.
13. Liu, C.-K., Latona, N. P., and Cooke, P. H.; Milling effects on leather. *JALCA* **102**, 191-197, 2007.
14. Liu, C.-K. and McClintick, M. D.; An energy approach to the characterization of the fracture resistance of leather. *JALCA* **92**, 103-118, 1997.
15. Tancous, J. J.; Skin, Hide and Leather Defects. Lee Corporation, Cincinnati, p. 13-14, 1986.